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A COMPOSITIONAL STUDY OF THE
MORPHOLOGY OF 18-ARMED POLY(STYRENE-ISOPRENE)
STAR-BLOCK COPOLYMERS

A Thesis Presented

By

Doreen Sue Herman

Submitted to the Graduate School of the
University of Massachusetts in partial fulfillment
of the requirements for the degree of

MASTER OF SCIENCE

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Polymer Science and Engineering

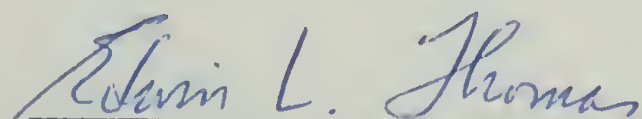
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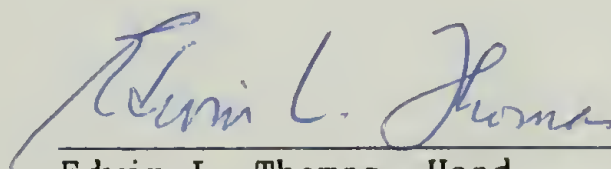
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ABSTRACT

A COMPOSITIONAL STUDY OF THE MORPHOLOGY OF 18-ARMED POLY(STYRENE-ISOPRENE) STAR-BLOCK COPOLYMERS

SEPTEMBER 1986

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This research explored the morphology of a series of 18 arm poly(styrene-isoprene) star-diblock copolymers as a function of the arm composition. Samples with composition increments of 10% polystyrene (PS) between 10 to 90% PS were examined with a closer look in the neighborhood of 30% PS. Samples were dissolved in toluene and slow cast into films 0.75 to 1.5 mm thick. Osmium tetroxide staining provided contrast of cryomicrotomed sections for examination with a JEOL 100CX transmission electron microscope. The ordered bicontinuous double diamond (OBDD) structure was observed for the 33 and 36% PS samples. All other samples exhibited those morphologies (spheres, cylinders or lamellae) expected for linear diblock samples of the same composition.

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C H A P T E R I

INTRODUCTION

Although much research has been done on the morphology, mechanical properties, compatability and general behavior of linear diblock copolymers, relatively little has been done on star diblock copolymers. These systems display small scale phase separation (on the order of the radius of gyration of individual blocks; 50 - 1000 Å) due to repulsive interactions between the chemically distinct block units. This micro-domain formation results in better dispersion and uniformity throughout the sample which enhances the mechanical behavior. For styrene-isoprene systems, the polystyrene domains act as physical crosslinks for the rubber. This type of crosslinking allows the material to sustain and recover from elastic deformation yet is reversible in the presence of heat and/or solvent for processing.

Many variables need to be accounted for in the study of star block copolymer morphology. These include the dependence on functionality (arm number), arm composition, molecular weight (MW), type of linking agent, casting solvent, and annealing conditions; the latter two directly related to the development of equilibrium structures. The MW affects the size and spatial arrangement of domains which are also a function of the volume fraction of the rubber phase. The goal of this work is to understand how the unique architecture of poly(styrene-isoprene) star-block copolymers is reflected in the observed morphology. Diblock systems are used as a frame of reference for comparison.

For AB diblock copolymers at near equilibrium conditions, the commonly accepted morphologies are those of spheres, cylinders or lamellae of the minor component in a matrix of the major fraction. As the volume fraction of the discrete phase (A) increases, the morphology consists of spheres of A up to approximately 20% A, when it changes to cylinders of A between 20 to 40% A and finally to alternating lamellae of A and B in the range of 40 to 60% A. Further increases in the A content result in a matrix reversal so that B becomes the discrete phase and the A phase now forms the matrix for the cylindrical and spherical domains. Figure 1.1 illustrates this phenomenon.

This thesis seeks to establish the equilibrium morphologies as a function of the composition for star diblock copolymers of constant arm number (18). Because of their more complex nature, this work constitutes only a beginning effort towards elucidating the various dependencies of sample microstructure on the star diblock copolymer architecture. The thesis is organized as follows. Chapter II reviews the pertinent background information on these systems. A summary of the synthesis, sample preparation and electron microscopy for the 18-arm poly(styrene-isoprene) star block copolymers to be studied appears in Chapter III. Chapter IV presents and discusses the results from the electron microscope investigation. Conclusions are drawn and suggestions for future work are made in Chapter V.

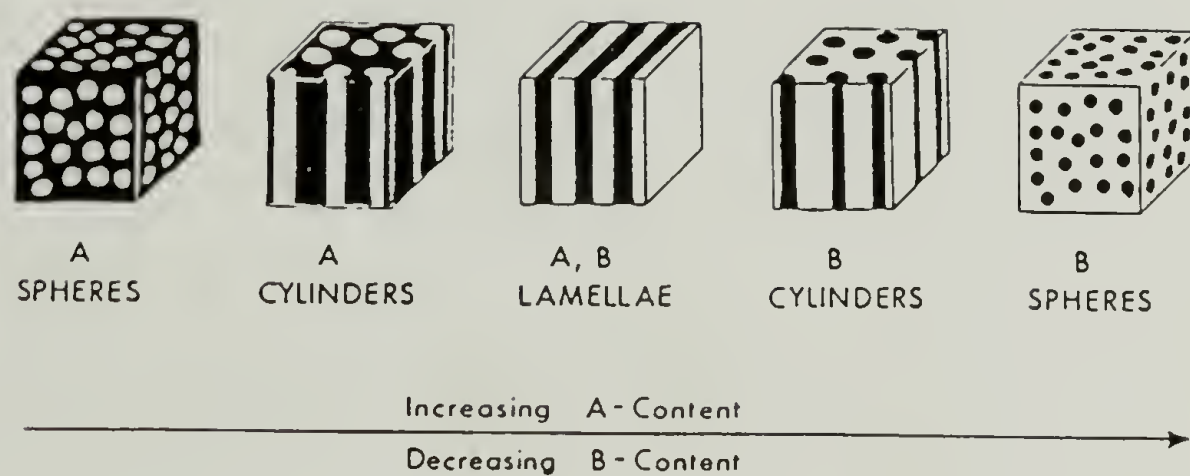


Figure 1.1 Block copolymer morphology as a function of composition.
From reference [2].

C H A P T E R I I

BACKGROUND

2.1 Opening Remarks

While a good deal of work has been done in the area of star polymers, the major thrusts have focused on the synthesis and solution behavior of star homopolymers. Much less attention has been given to the synthesis, solution and solid-state behavior of star-block copolymers. Star copolymer research is an extension of the widely studied field of linear block copolymers. Many analogies, in regards to morphology, can be drawn between these two areas of study even though there is much to be learned about star systems while linear materials are fairly well characterized to date [1,2,3,4,5].

The synthesis of well controlled block copolymers became a more exact science with the technique of anionic synthesis [6]. With cationic or free radical synthesis, chain transfer and elimination reactions promoted polydisperse polymers. Anionic polymerization enabled linear and monodisperse copolymer chains to be synthesized. Anionic reactions are not without difficulties as they are exceptionally sensitive to contaminants in the air, reaction vessel or starting materials. Careful techniques can generally assure polydispersity values of M_w/M_n less than 1.1 as determined by GPC [7,8,9,10].

2.2 Star Homopolymers

Star shaped molecules are produced in a two stage process. The diblock arms of the star are anionically synthesized to create living arms. These in turn are reacted with multifunctional linking agents to form stars of varying arm numbers depending on the amount and type of linking agent. Divinyl benzene (DVB) and halogenated compounds form the two general types of linking agents. In either case, the first step is the anionic synthesis of diblock arms followed by addition of linking agent to form stars. Fractionation of the final product is necessary regardless of linking agent to remove unreacted arms and partially formed stars.

When linking with DVB, the arms are allowed to react to the desired molecular weight before adding the DVB. Some block chain ends react with the DVB to form a microgel linking center and provides additional reactive vinyl groups. More arms then react with these pendant vinyl groups to form star shaped molecules. The functionality of these stars depends mainly on steric considerations, which themselves are a function of polymerization conditions. Higher functionality can be obtained by increasing the ratio of DVB added, hence creating more active centers. Higher functionality can also be achieved by lowering the arm molecular weight, increasing the arm concentration and raising the meta to para ratio of the DVB [11,12]. As arm number increases, dispersity of the molecules generally does as well. In addition one would expect that the structure of the core of the star could have a

large effect on functionality and steric factors. To date, very little is known about the actual star core structure.

Halogenated linking agents offer several advantages over DVB. The type that will be used in this study are chlorosilanes although there are non-silinated types. There are several good references on the subject [13,14,15,16,17,18].

The reaction mechanism which occurs with halogenated linking agents is that of metathesis whereas DVB employs an addition reaction. During the metathesis reaction, a charged living polymer arm displaces an electronegative species on the neutral linking agent. Several non-silinated linking agents [12,19,20,21,22] were found to be very sensitive to polymerization conditions [23]. The tendency for metal halogen interchanges to occur results in active linking agents and inert polymer arms. If the active linking agents react with other linking sites, the functionality becomes rather difficult to control. In order to achieve desired dispersity, the temperature of the reaction needs to be carefully maintained as does the order of reactant addition. As mentioned earlier, fractionation is needed for narrow polydispersities.

The use of chlorosilane linking agents enabled stars to be synthesized with better defined functionalities. Early work with halogenated linking agents centered on star homopolymer synthesis. In the 1960's, Morton et al. [24] used silicon tetrachloride to produce 3- and 4-armed polystyrene stars. After recognizing that steric factors were hindering increasing arm number due to limited mobility, Zelinsky [25] polymerized living polybutadiene with SiCl_4 and CH_3SiCl_3 . Roovers

and Bywater in 1972 [26] related steric problems to polystyrene stars with more than two arms. They were able to synthesize 4-armed stars using 1,2-bis(methyl-dichlorosilyl)ethane.

Two years later, the same authors [27] produced a 6-armed polystyrene star utilizing 1,2-bis(trichlorosilyl)ethane. They made the important observation that by adding a small amount of butadiene to the living polystyrene arms, overcrowding at the star core was alleviated. Gervasi et al. [28] had noted this same peculiarity in 1966 at which time they concluded that small amounts of rubber were needed in order to attain functionalities of four or more.

Hadjichristides and Roovers [29] synthesized 4- and 6-armed polyisoprene stars in the mid 1970's and later produced 8- and 12-armed stars using tetra(methyl-dichlorosilyl)ethane silane and tetra(trichlorosilyl)ethane silane respectively [30]. Light scattering, membrane osmometry and GPC performed on the precursor arms as well as the polyisoprene stars confirmed the functionality.

When Hadjichristides and Fetters synthesized 18-armed polyisoprene stars in 1980 without first encapping the arms with polybutadiene, they concluded that the encapping increased the reaction rate but had no effect on the functionality [31]. Roovers et al. [32] in 1983 followed up on the previously stated work by producing an 18-arm star of polystyrene endcapped with polybutadiene using octadeca-chlorosilane as the linking agent.

The use of chlorosilane linking agents has enabled chemists to produce stars with high (5) arm numbers and consistently well defined

arms number and arm length. One drawback of the chlorosilane linking agents which should be recognized is that they may in fact augment steric problems at the core due to their small size in relation to DVB microgels.

2.3 Star-Block Copolymers

Star-block copolymer synthesis and solid state morphology have been given less attention than solution and melt behavior of star homopolymers since the later material had been suggested as model systems for branched materials. The variation in synthesis rests in the living diblock arms. Rather than a one step reaction as needed for homopolymers, the diblocks are made in a two step process.

The synthesis and morphology of diblock, triblock, 3- and 4-armed stars was reported by Price et al. [33] in 1972. Dichlorodimethyl-, trichloromethyl-, and tetramethyl silane were the linking agents for the triblocks and stars. Volume percent styrene was kept constant at 24% while the morphology as a function of arm number was investigated. Solvent cast thin films of all of the samples showed hexagonally packed polystyrene cylinders in a polyisoprene matrix. These results matched those seen for the corresponding di- and triblocks. In addition, they concluded that arm number had no effect on domain diameter or spacing for the samples studied.

Bi et al. [34] found contradictory results while observing similar samples which had been synthesized using DVB. The stars had from six to

ten arms of styrene tipped with isoprene. Volume percent polystyrene was kept near 28%. Morphologically, they saw a body centered array of spherical polystyrene domains in a polyisoprene matrix. To explain the discrepancy, Bi et al. concluded that the morphology they saw was that of the (111) projection of a body centered cubic (BCC) lattice while Price et al. were in fact seeing an overlap of spherical domains.

Bi and Fetters [35] reexamined the structure of 6- and 9-armed DVB linked stars to understand the apparent difference. Rather than rely on a single image, they observed several projections from various regions. In this way, by comparing the relative distances between domains of the different angles and the volume (area) they occupied to the actual composition the structure was determined to be a BCC array of polystyrene spheres in a polyisoprene matrix. It should be remarked that studies of this type are of somewhat limited use due to variations within a given sample as a result of the compression and deformation associated with microtoming. Therefore, care must be taken to ensure that the same area of the sample be viewed for the entire tilt series.

Pedemonte et al. [36] studied Europrene T-162, a commercially available 4-armed star manufactured by the Anic Company. These 50:50 stars were linked using tetrachlorosilane with butadiene at the core and styrene at the tips. Compression molded films were made to study the morphology in three directions. They concluded that short rods of polystyrene were aligned perpendicular to the plane of compression in as-molded films. These rods then become parallel to the plane of compression and re-orient in the direction of stretch when the material

is tested in tension. On examining their micrographs of the as-molded films there appears to be little obvious differences between the three directions. In addition, the structures closely resembled those seen for diblocks of similar compositions which had formed under non-equilibrium conditions.

Bi and Fetters [37] later expanded on their previous work to include the synthesis and morphological investigation for a series of DVB stars. The styrene-butadiene and styrene-isoprene stars contained 30-35% polystyrene with from 3 to 29 arms. The styrene-butadiene stars formed a spherical morphology with the styrene as the discrete phase. Through their studies, they concluded that solvent had no effect on the formation of microstructure in cast films and that annealing promoted little change in structure.

Kinning [38] found entirely different results on the effect of solvent. By purposely choosing cyclohexane (a preferential solvent for isoprene) on poly (styrene-isoprene) stars with 30% polystyrene as the outer block and styrene arm molecular weight of 10,000 a phase transformation was induced, resulting in a non-equilibrium morphology for 6- and 8-armed stars. The microstructure seen (cylinders) corresponded to the morphology expected for a sample with a greater percentage of isoprene. The preferential solvent swelled the isoprene phase resulting in an apparent increase in the percentage of isoprene. An annealing treatment brought the system into its equilibrium state, at which time the material displayed the morphology expected for that composition as discussed below.

Kinning's work on solvent effects was an extension of previous work on star-diblock copolymers done by Alward et al. [39]. They studied the effect of arm number and arm molecular weight on the morphology of poly (styrene-isoprene) star block copolymers. Most samples contained 30% polystyrene as the outer block with 2 to 18 arms, and total arm molecular weights of 23,000, 33,000 or 100,000. For low arm number stars, the cylindrical morphology was seen as would be expected from linear block copolymer behavior for this composition. A new and distinct morphology referred to as the ordered bicontinuous (OB) was reported for stars consisting of 8 or more arms at 33,000 arm molecular weight, 12-armed stars in the mid and high range molecular weights and for all 18-armed stars studied.

The OB morphology appears between the cylindrical and lamellar domain structures. Stars with styrene cores and 30 wt% isoprene outer blocks (inverted stars) also display this morphology [38]. This new morphology was believed to be induced by the unique constraints imposed on the stars through the central linking site. The forces to be balanced here include overcrowding at the star core resulting in a radial arm projection and the requirement that the styrene-isoprene junction be at the domain boundary. Energy minimization here becomes a function of conformational restrictions for junction placement and inner block location, maintenance of constant density, and surface area to volume ratio. Recently such a morphology was noticed in linear polystyrene-polydiene diblock copolymers with 62-66 volume percent polystyrene [38,40].

Micrographs of the OB structure show more areas of high contrast than seen with other morphologies. At least five grain regions of high contrast were reported [39]. One of these projections, the "wagon wheel" had been published by Aggarwal [41] in 1976 for a 12-armed DVB linked star with 30% polystyrene and arm MW of 71,000. The appearance of more than two types of high contrast areas indicated higher structural symmetry than that of the cylindrical morphology which exhibits only two well defined projections (hexagonally packed spheres when viewed as a cross section of the cylinder, and lamellae when projected normal to a cylinder axis). Tilting experiments in the microscope stage on a sample displaying the OB morphology confirmed that all projections derived from a single structure in the sample.

Several conclusions were drawn. For 4-arm stars exhibiting cylindrical morphology and 18-arm stars showing OB morphologies, the interdomain distance was seen to widen with an increase in arm molecular weight. Transitions between cylindrical and ordered bicontinuous structures were noted to be between 12 and 18 arms for the 23,000 MW series, 4 and 8 arms for 33,000 MW series and between 4 and 12 arms for the 100,000 MW series. Further studies on the arm number dependence for poly(styrene-isoprene) stars with 30% polystyrene and polystyrene molecular weight of 10,000 showed that a distinct morphological change from cylinders to the OB structure occurred between stars having 5 and 6 arms [42].

Early analysis of the OB structure by Handlin et al. [43] suggested a FCC arrangement of polyisoprene spheres in a polystyrene

matrix. The observed morphology in particular, the "wagon wheel" projection was believed to be a result of the overlap of two such layers. However, this structure did not successfully account for all projections observed. Alward [44] attempted to better describe the newly discovered morphology by proposing a model consisting of an ordered bicontinuous network, consisting of an FCC lattice and tetrahedrally coordinated arrays of short polystyrene rods as the basis. This better suited the data but had shortcomings with respect to the geometrical relationships expected to be seen between various projections and with details of the peak positions in the small angle x-ray data.

Further analysis of this new morphology has resulted in a reliable detailed structural model for this system. Working with Alward's hypothesis that the lattice was bicontinuous, had cubic symmetry, and that the angle between polystyrene branches was $\sim 120^\circ$ an ordered bicontinuous double diamond structure was proposed by Kinning [45]. This model was supported not only on the basis of transmission electron microscopy (TEM) but most importantly by data from small angle x-ray scattering (SAXS), and computer generated projected images. The resulting structure "consists of two distinct, mutually interwoven but unconnected, three dimensional networks of polystyrene, each of which exhibits the symmetry of a diamond lattice, surrounded by a continuous polyisoprene phase." [45].

2.4 Practical Considerations

Several authors have investigated the mechanical behavior of stars in comparison to similar linear di- and triblock materials. Generally, stars exhibit greater yield strength, have higher tensile strength, smaller extension ratios and less permanent set. Pedemonte's [36] conclusion of polystyrene rods aligned perpendicular to the plane of compression hold practical value in explaining the necking and strain softening seen during mechanical testing.

Meyer and Widmaier [46] examined the adhesive behavior of 2- to 13-armed stars with di- and triblock arms. The diblock arms contained 50% polystyrene while the triblock arms were made of 70% polystyrene. The linking agents were DVB, silicon tetrachloride- and 1,2 4,5-tetrakis(chloromethyl)benzene. The stars were found to be better adhesives than linear complements. This increase in cohesive strength was ascribed to the physical crosslinks of the rubber components along with the formation of a large glassy domain of polystyrene and DVB at the star core.

Some processing/property relationships on commercially available materials were analysed by LeBlanc [47]. Solprene[®], registered trademark of the Phillips Petroleum Company, a 4-armed star, was compared to Shell's Kraton[®] triblock rubbers. The star materials again showed a higher Young's modulus and greater tendency to yield. Properties such as modulus, yield stress/strain and ultimate

stress/strain showed a greater molecular weight dependency for the star molecules.

Star copolymers displaying the OB, later called OBDD, structure were reported to have greater tensile moduli than similar samples displaying a cylindrical morphology [38]. The Young's modulus was nearly an order of magnitude larger and was attributed to the enhanced continuity of the polystyrene phase.

A clear picture of the solid state structure and behavior of these star branched materials has yet to be developed. This thesis focuses on the solid state morphology at constant arm number (18) with variable arm composition. The composition range was chosen to explore a wide span (10 to 90% polystyrene), with a more detailed look at the compositional range surrounding the newly seen OBDD structure (27, 33 and 36% polystyrene).

C H A P T E R I I I

EXPERIMENTAL

3.1 Synthesis

Samples of 18-armed star block copolymers were generously provided by Dr. Lewis J. Fetters of Exxon Research and Development. The styrene/isoprene diblock star arms consist of a core of isoprene with styrene as the outer block. Compositions in the range of 10 to 90% styrene were provided. Decaoctachlorosilane was used as the linking agent for all of the 18-armed stars. All purifications and reactions were done under high vacuum. Reactions were carried out in benzene with sec-butyllithium as the initiator. The two stage arm syntheses were performed at 30C and the linking step at 50C. Degassed methanol was used to terminate the reaction. Fractionation followed to separate any unreacted arms from the star molecules. Number average (M_n) and weight average (M_w) molecular weights were determined by high speed membrane osmometry and light scattering respectively for the living arms as well as the stars. Gel permeation chromatography (GPC) enabled the molecular weight polydispersity to be assessed. More details on the synthesis and purification procedures can be found in the original work [30,31].

Table 3.1 displays the samples to be analyzed in this study. Each sample is designated by three numbers. The first number refers to the number of arms in the star molecule, the second to the percentage of polystyrene in the diblock arm and the last number is the number average molecular weight of the polystyrene component of an arm divided by 1000.

TABLE 3.1 TABLE OF STAR BLOCK COPOLYMER SAMPLES

SAMPLE	MW PS	MW PI	ARM MW	TOTAL MW
18:10:10	10,000	90,000	100,000	1,800,000
18:20:10	10,000	40,000	50,000	900,000
18:27:12	12,000	32,000	44,000	800,000
18:30:10	10,000	23,000	33,000	600,000
18:33:10	10,000	20,000	30,000	550,000
18:36:10	10,000	18,000	28,000	500,000
18:40:10	10,000	15,000	25,000	450,000
18:50:10	10,000	10,000	20,000	360,000
18:60:26	26,000	17,000	43,000	800,000
18:70:30	30,000	13,000	43,000	800,000
18:80:30	30,000	8,000	38,000	700,000
18:90:30	30,000	3,000	33,000	600,000

Also shown in this table are the polyisoprene molecular weight, arm molecular weight and the total molecular weight of the star. Figure 3.1 explains the sample designation and shows a schematic diagram of a star-diblock copolymer molecule.

3.2 Sample Preparation

The samples were dissolved in toluene, a non-preferential solvent as defined by solubility parameters (δ PS = 9.1, δ PI = 8.15, δ Toluene = 8.9). Less than 0.25% Irganox 1010 antioxidant was added to prevent crosslinking and oxidation of the isoprene phase during annealing. Solutions of 5 wt% polymer in solvent were prepared to cast films 0.75 to 1.5mm thick and 3 cm in diameter. Solutions were poured into the specially constructed casting dishes consisting of flat glass plates fused to two inch glass cylinders. Before use, the dishes were rinsed with toluene and treated with dimethyl-dichlorosilane (a release agent) to facilitate sample removal. Two casting methods were utilized in order to obtain the best long range order possible.

For the first technique, the casting dishes were covered with three inch petri dish covers supported by toothpicks. This was done to control the solvent evaporation rate. The covered dishes were left in a hood to evaporate at room temperature. After two to five days all samples were sufficiently dry. Samples were placed directly into the vacuum oven under full vacuum to anneal at 120C for one week.

SAMPLE DESIGNATION
18:27:12
18= NUMBER OF ARMS 27= WEIGHT PERCENT POLYSTYRENE 12= MOLECULAR WEIGHT OF PS BLOCK DIVIDED BY 1000

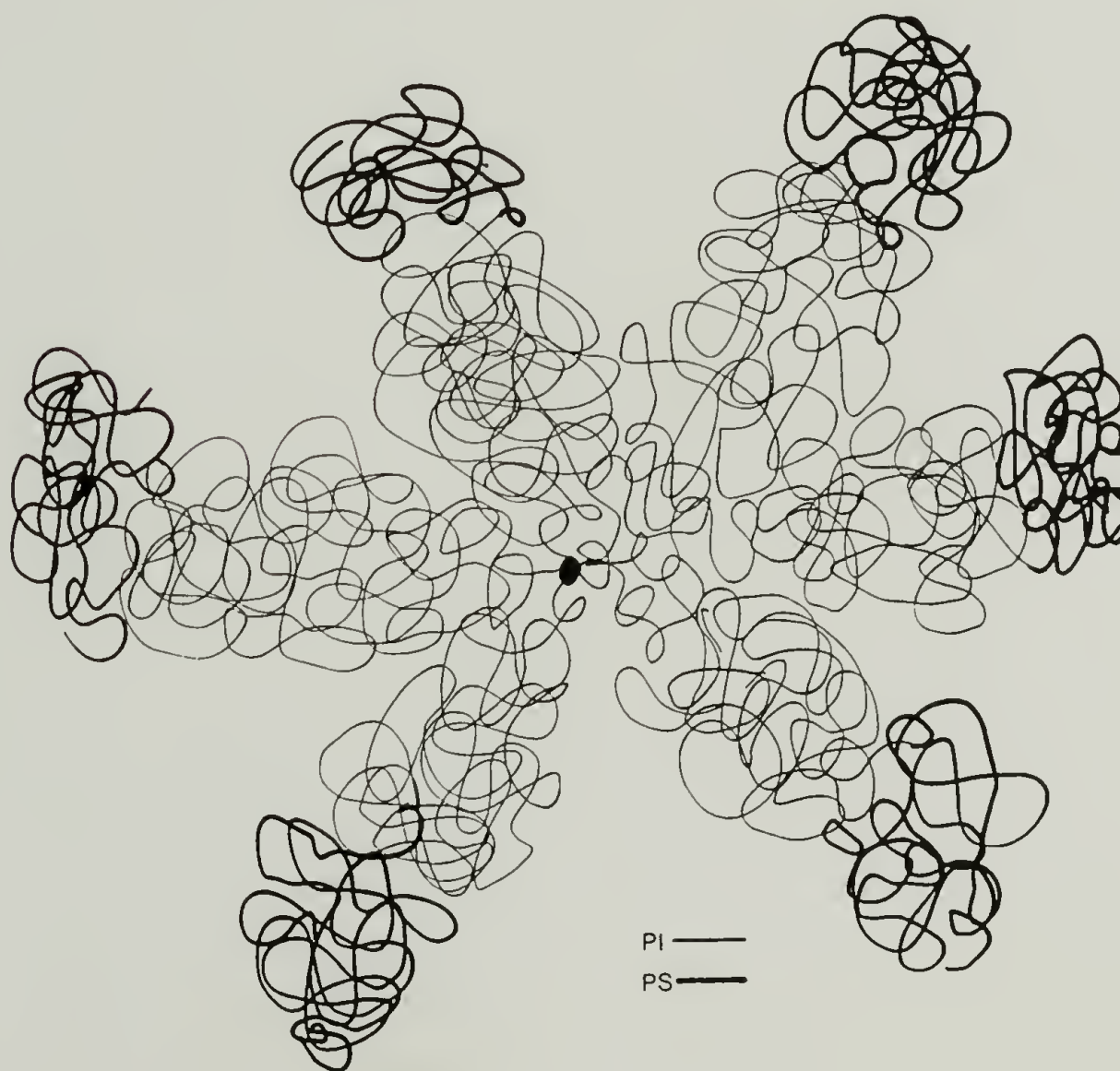


FIGURE 3.1 Sample code and schematic of star molecule in cross section.

In order to promote equilibrium structure formation, an alternate procedure was used to provide a more controlled solvent evaporation rate. The temperature was also somewhat elevated to increase molecular mobility during the casting process. Two groups of three casting dishes were placed directly in the vacuum oven. Each group of casting dishes was placed directly under a cover consisting of a six inch glass petri dish with two 0.1 mm vent holes per casting dish. The oven was maintained at 65C with the purge valve open and a water aspirator attached to the vacuum line. This was done to provide a continuous air purge to remove solvent vapors. Within five days the solvent evaporated and the oven temperature was raised to 80C. The purge valve was also closed to provide a low vacuum to slowly draw off any residual solvent. Low vacuum and gradual temperature increases were used to avoid foaming of the samples with high styrene content as the toluene evaporated. After one day the vacuum pump was connected and the temperature raised to 120C over the course of three days. The samples were left to anneal for one week under these conditions.

An AO Reichert Ultracut microtome with FC4 cryo-attachment was used to prepare thin (400 to 1000Å) sections suitable for transmission electron microscopy. The sample and knife temperatures were maintained at -110C, well below the T_g of the isoprene phase. The material to be sectioned was cut into a triangle about 2mm X 2mm X 2mm and attached with instant glue to a small aluminum mounting stub. Histo-prep[®] embedding medium was placed on both sides of the sample to add support. Both glass and diamond (Diatome Company) knives were used. A wet knife

technique utilized N-propanol to float the sections, which were then directed onto 800 mesh copper grids with an eyelash. Cut sections were exposed to osmium tetroxide vapors for 3 hours to selectively stain the isoprene component and enhance contrast.

3.3 Electron Microscopy

A JEOL 100CX TEMSCAN electron microscope was utilized in the bright field mode to observe the samples. Operating conditions of 100KV, with 100 micron condensor lens and 50 micron objective lens apertures were most commonly employed. A side entry goniometer and single tilt holder enabled sample grains to be viewed over tilts $\pm 60^\circ$. Beam damage due to charging and heating effects of the electron beam, residual stresses from sectioning, and variations in sample thickness and in stain density appeared as curling and dimensional changes in the sample. These effects could be minimized by first exposing the specimen to the beam at crossover conditions and 5,000X magnification for one minute before bringing the microscope up to the desired magnification (usually 20-33,000X). Micrographs were recorded on Kodak SO-163 film plates.

C H A P T E R I V

RESULTS AND DISCUSSION

The results of this preliminary survey of the morphology of star block copolymers as a function of the arm composition are fascinating yet incomplete. While most samples show unmistakable morphologies, others show less well defined order. When viewing the micrographs that follow, the reader is reminded that the dark areas represent the isoprene phase which has been selectively stained by osmium tetroxide. All photographs appear at the same magnification. Domain sizes were estimated from the micrographs and appear in Table 4.1.

For diblock copolymer systems, the domain dimension (D) and interdomain distance (d_{int}) have been predicted to scale according to equations 1 and 2 where M_d is the MW of the domain forming block and M is the total copolymer MW.

$$D = C_1 M_d^a \quad 4.1$$

$$d_{int} = C_2 M^a \quad 4.2$$

Values of $a = 0.56$ and $a = 0.67$ have been predicted by Meier and Helfand respectively. Comparison to experimental results find Helfand's theory to match most closely for lamellar and cylindrical morphologies while the measured spherical microstructures generally tend to be smaller than predicted [5].

The domain measurements given in Table 4.1 are for the spherical, cylindrical and lamellar morphologies. The cylinder diameter measurements are an average of the axial and longitudinal views for the

TABLE 4.1 MEASURED DOMAIN SIZES FOR 18-ARMED
STAR BLOCK COPOLYMERS

SAMPLE	DOMAIN SIZES		
	SPHERE	CYLINDER	LAMELLAR
18:10:10	130 A PS	---	---
18:20:10	---	100 A PS	---
18:27:12	---	100 A PS	---
18:40:10	---	---	60 A PS 90 A PI
18:50:10	---	---	60 A PS 100 A PI
18:60:26	---	---	125 A PS 80 A PI
18:70:30	---	90 A PI	---
18:80:30	---	70 A PI	---
18:90:30	140 A PI	---	---

minority component. As the MW increases, the mobility of the molecules in solution and more importantly in the solid state decreases. In the case of 18-armed stars, the added physical entanglements between the large number of arms further hinders the formation of ordered equilibrium structures. Some samples showed many small areas of highly developed order interspersed between areas of poor or no order. There seemed to be no difference between the development of order for the two annealing methods used in this study.

Figure 4.1 is a molecular schematic depicting the lamellar morphology for a styrene-isoprene 18 arm diblock star.

The 18:10:10 sample shown in Figure 4.2 exhibits irregular spherical domains which do not show much long range order. These spheres have average diameters of about 130Å. Since the material did not in general develop good long range order, different sections showed variations in domain sizes. The lack of long range order may be related to the very high MW of this sample (1,800,000).

The 18:20:10 sample in Figure 4.3 shows two types of ordered areas which appear as hexagonally close packed spheres and lamellae. These in fact represent the axial and longitudinal cross sections of cylinders. This is typical of materials displaying the cylindrical morphology. In order to distinguish this structure from that of spheres or lamellae, both projections must be visible. Since each cut section reveals many randomly oriented grains, the likelihood of seeing both lamellae and spheres coexisting is great. Alternatively, the specimen can be tilted in the microscope to cause a change from the axial projection (spheres)

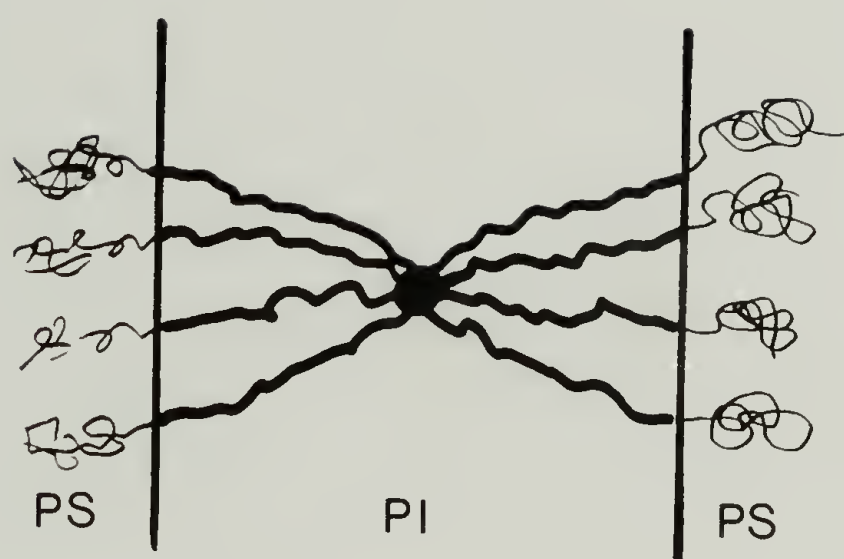


FIGURE 4.1 Schematic of a star-diblock copolymer forming a lamellar morphology.

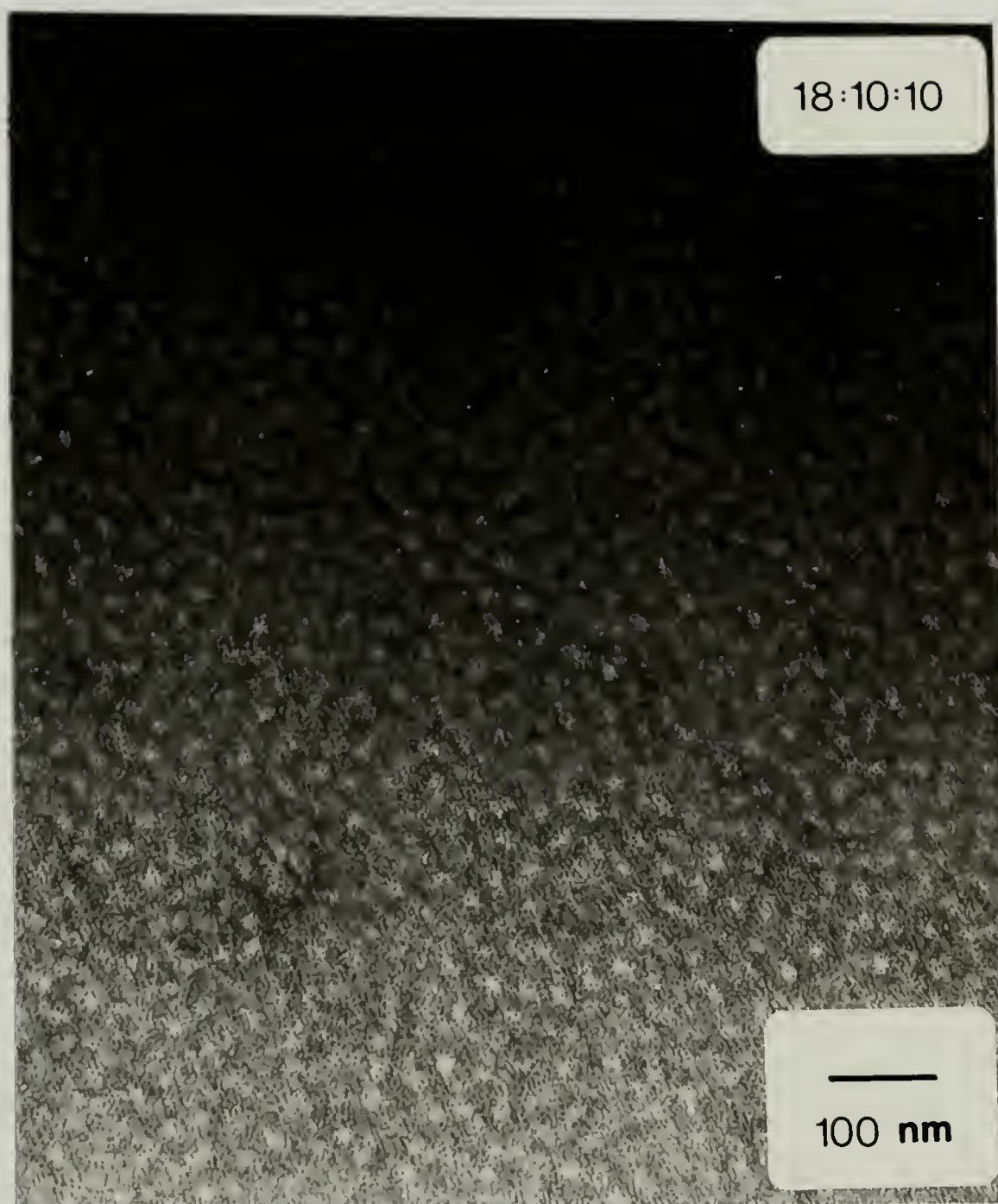


FIGURE 4.2 18:10:10 sample displaying disordered array of polystyrene spheres.

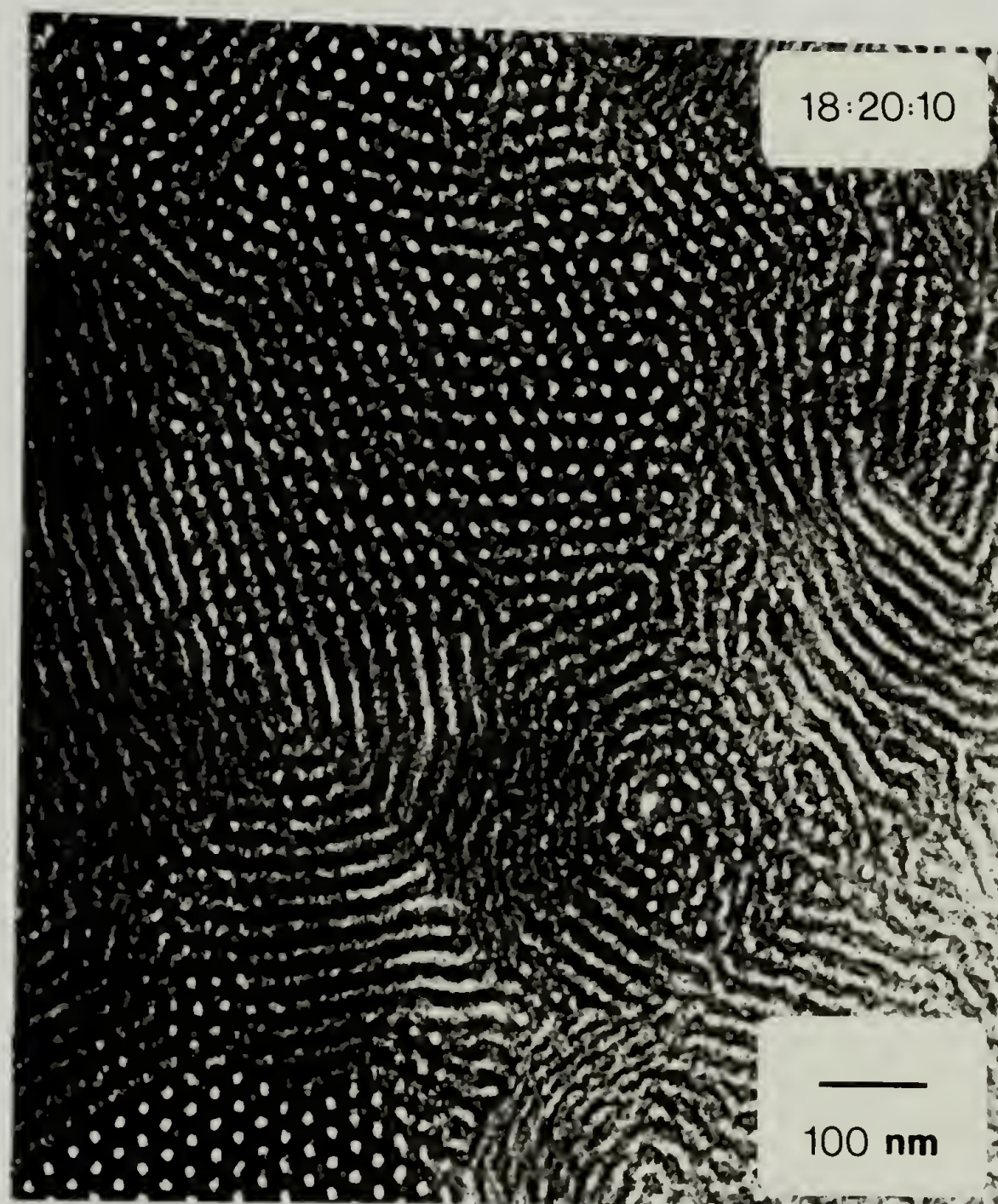


FIGURE 4.3 18:20:10 sample showing cylindrical morphology.

to the longitudinal (lamellae) projection. The gray low contrast areas are those projections which have not been cut normal to or along the cylinder axis.

The 18:27:12 sample shown in Figure 4.4 also formed a cylindrical microstructure. A tilt series for this sample is shown in Figures 4.5 and 4.6 in which the sample has been tilted over a range of 60°. The axis of tilt falls approximately on the diagonal from the lower right hand corner to the upper left of the micrograph. The marked area displays the projected morphological variations mentioned above. One can see how the lamellar-like structure in Figure 4.5 converts into a spherical domain in Figure 4.6.

The 18:30:10 sample was previously studied and its structure has been documented as the ordered bicontinuous double diamond [44,45]. This morphology shows several highly ordered projections. At least six were previously seen and confirmed through computer simulation of the OBDD structural model [38,44,45].

The 18:33:10 sample shows many interesting features (see Figure 4.7). Some regions show grains characteristic of the OBDD structure. The outlined region for instance has been referred to by Alward [44] as the "barber pole" projection. After viewing a large area of several sections of this sample it was concluded that the morphology most resembles the OBDD although not all of the expected projections are seen. The overall high contrast seen is characteristic of the double diamond structure. Some type of order is apparent in all areas of the micrograph and very few regions show a uniform gray level. A

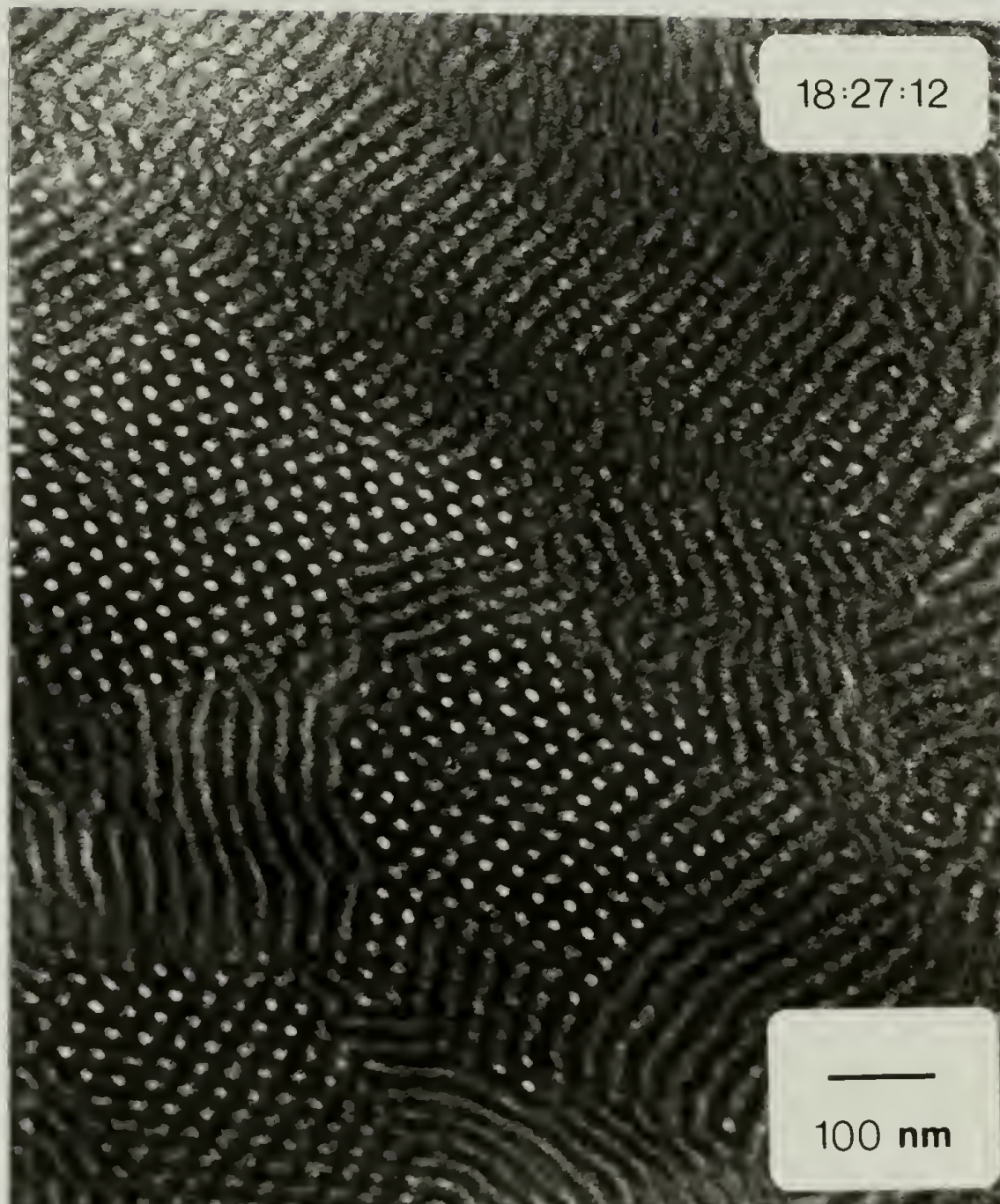


FIGURE 4.4 18:27:12 sample displaying a cylindrical microstructure.

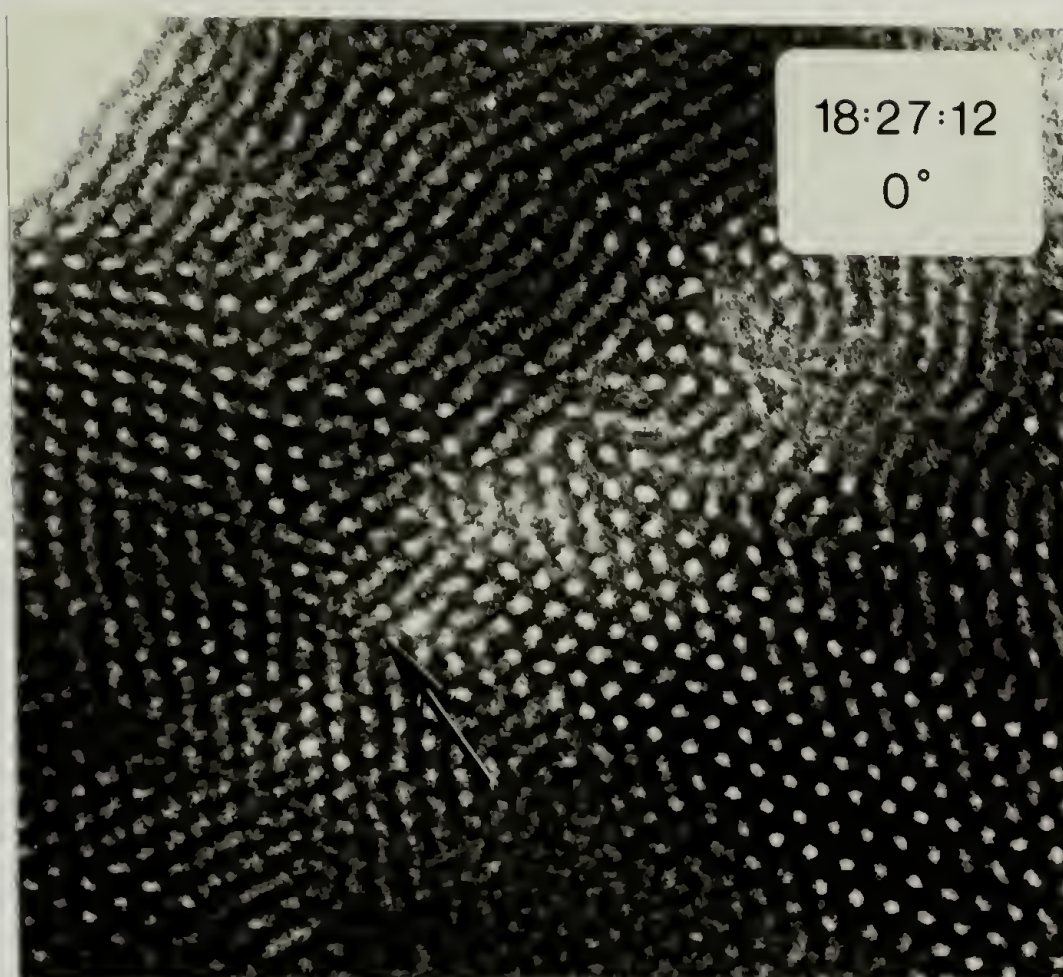


FIGURE 4.5 18:27:12 sample showing lamellar-like structure.

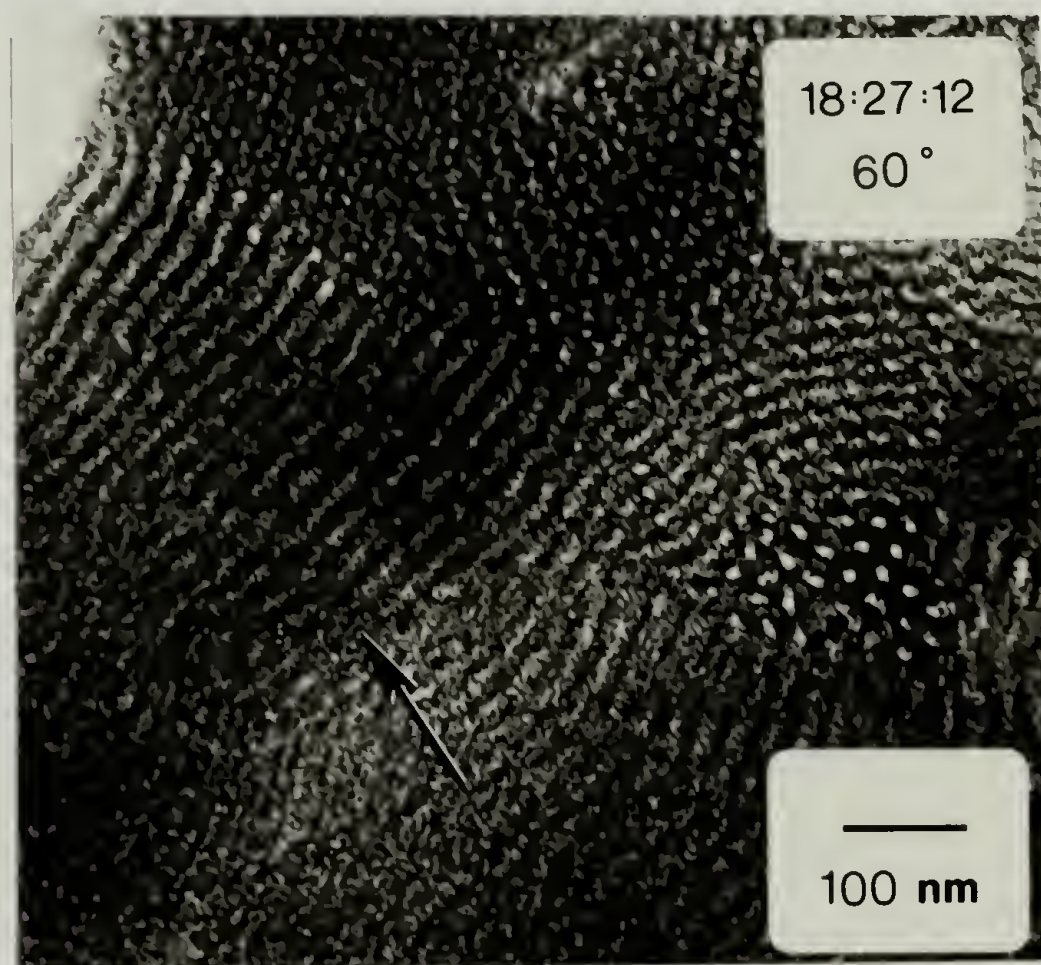


FIGURE 4.6 18:27:12 sample tilted 60° to confirm cylindrical morphology. Arrows indicate grain in which approximately longitudinal view changes to an axial view after tilt.

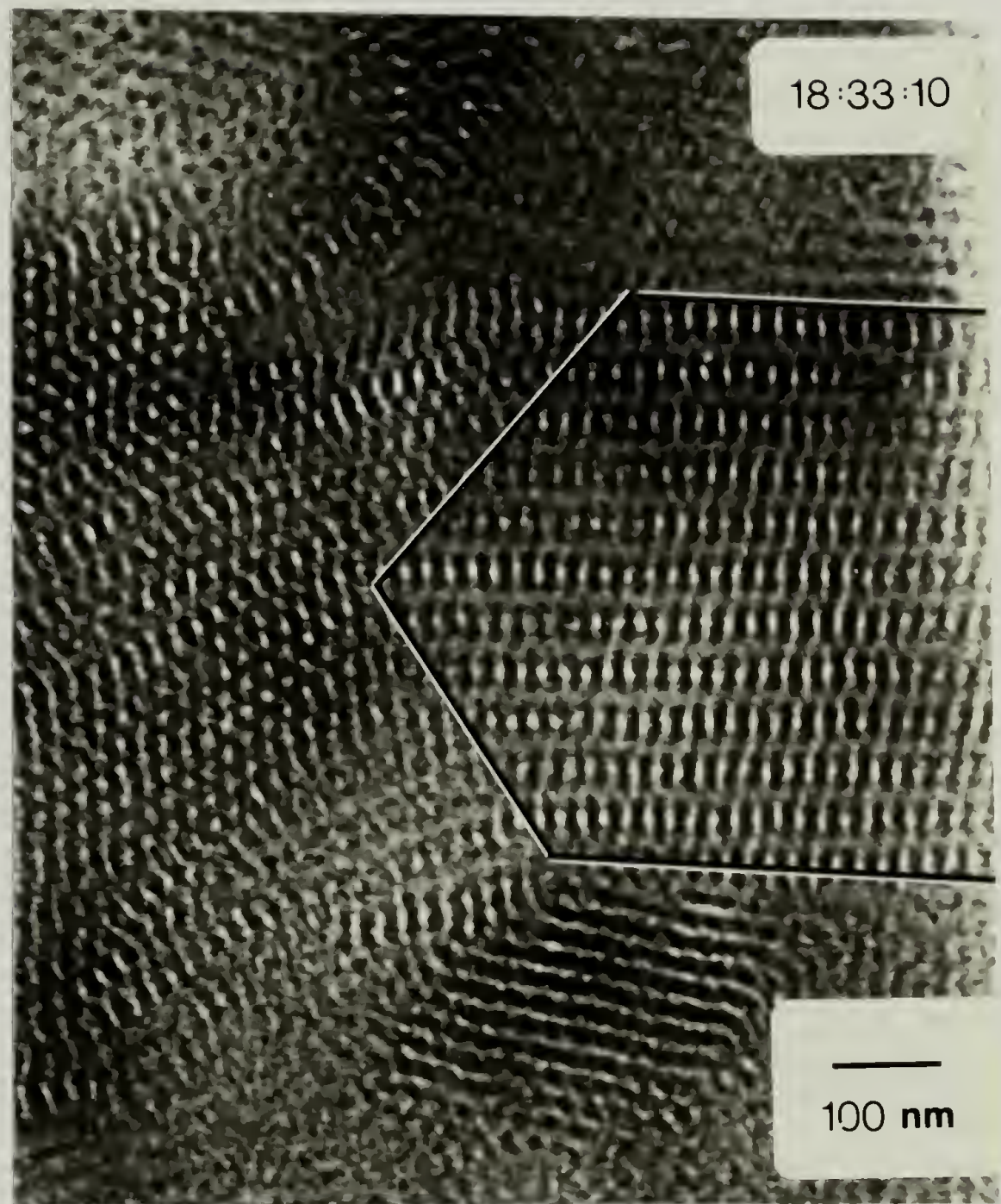


FIGURE 4.7 18:33:10 sample showing an OBDD structure which is not highly ordered.

cylindrical structure such as Figures 4.3 and 4.4 shows more uniform gray areas. The ordering for this particular sample is somewhat poor, hence the distinctive lack of the familiar "wagon wheel" projection.

The 18:36:10 in Figure 4.8 clearly shows an ordered OBDD structure. This sample shows all of the grains previously seen for this morphology including the "wagon wheel" (A) corresponding to the (111) projection and the "square" (B) corresponding to the (100). Many well defined grain boundaries can be identified in the micrograph. Contrast is high in all areas.

Further increases in the styrene content induce a transition to alternating lamellae of styrene and isoprene as seen for the 18:40:10, 18:50:10 and 18:60:26 samples shown in Figures 4.9, 4.10, and 4.11 respectively. All projections of these samples showed either lamellar structures or areas of gray indicative of a section cut parallel to the domain boundary. The variation in lamellar thickness is due to the angle at which the sample is cut. The wider lamellae are cut orthogonal to the domain boundary resulting in high contrast and sharply defined boundaries. This can be explained in terms of constructive overlap. As the cutting surface is tilted, a boundary zone develops which appears as a gray region in the micrograph because the electron beam must travel through overlapping regions of styrene and isoprene. As the degree of tilt increases, the lamellae appear thinner until they disappear to a constant gray level.

Figure 4.12 shows the cylindrical morphology seen in the 18:70:30 sample. Note that the contrast is reversed from the 18:27:10 sample

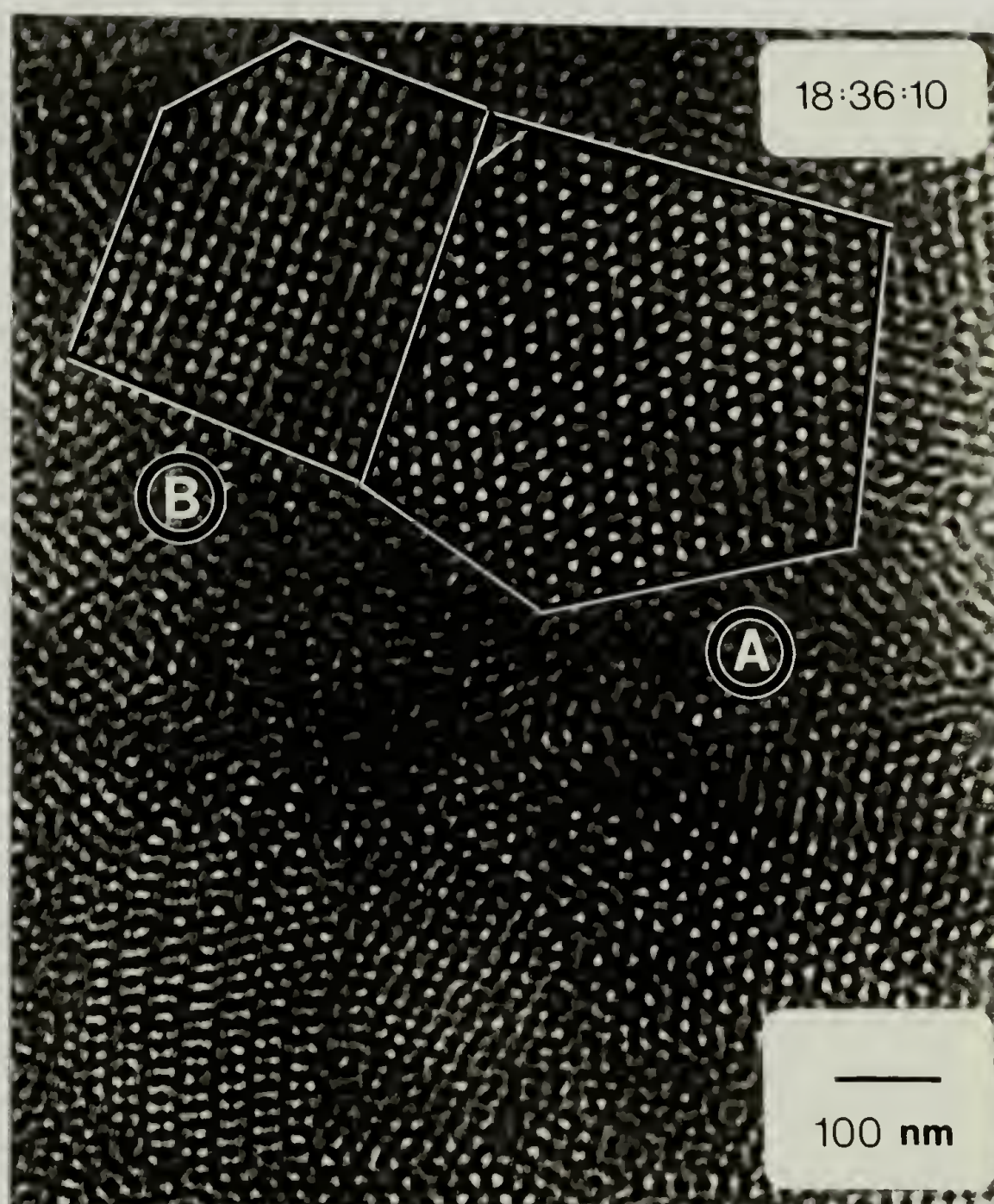


FIGURE 4.8 18:36:10 sample showing well ordered OBDD structure.

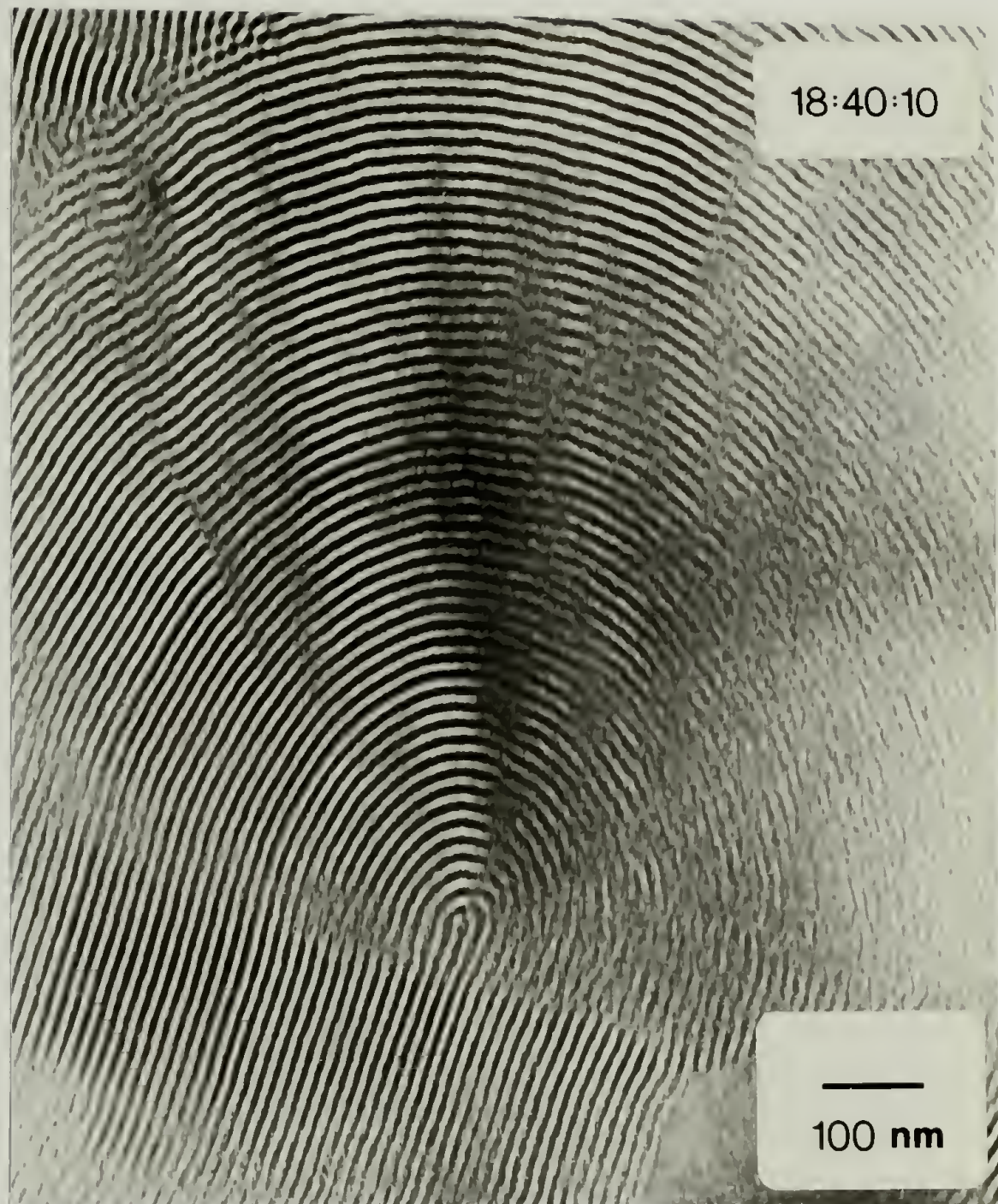


FIGURE 4.9 Lamellar morphology as seen in the 18:40:10 sample.

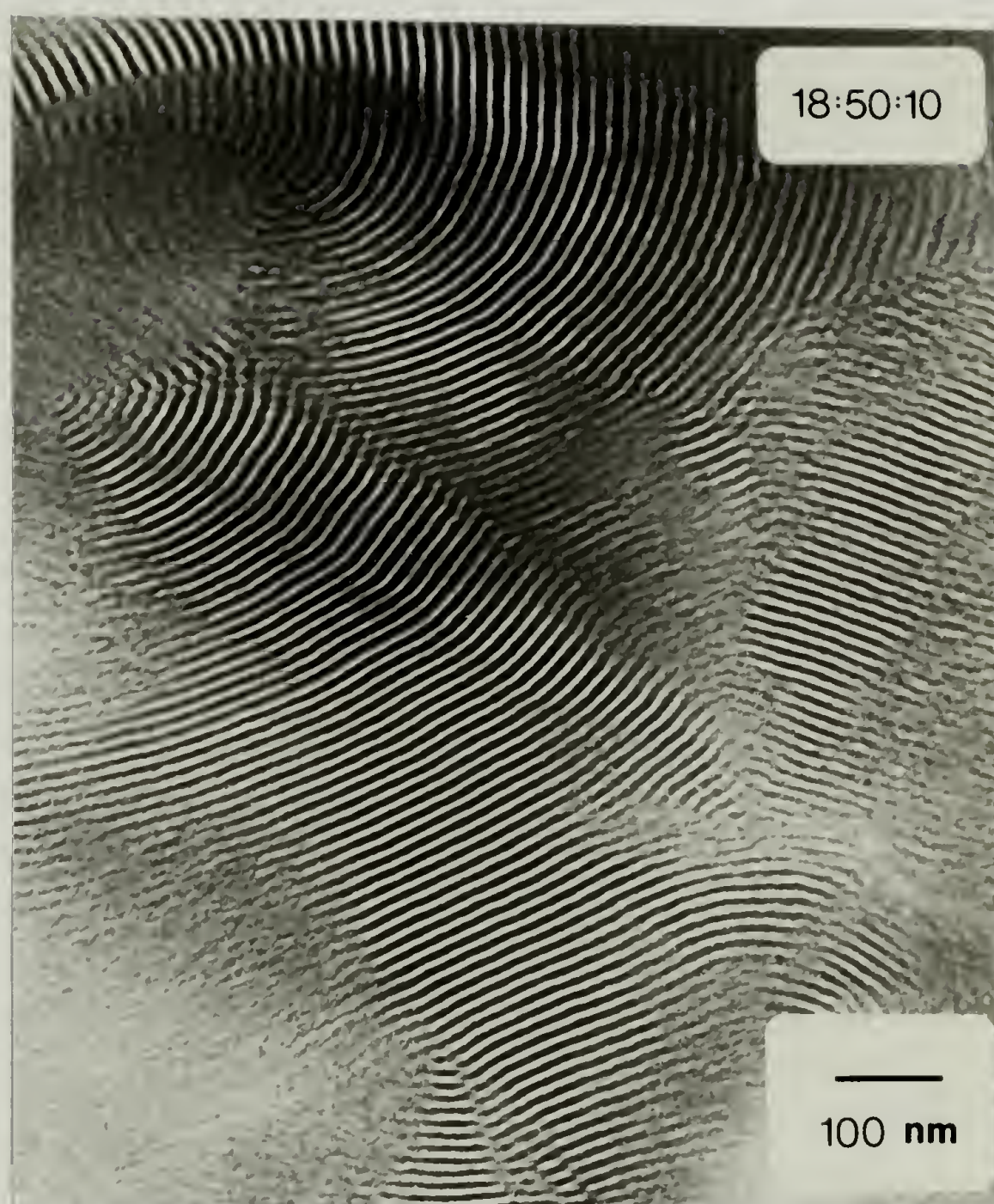


FIGURE 4.10 18:50:10 sample showing lamellar microstructure.

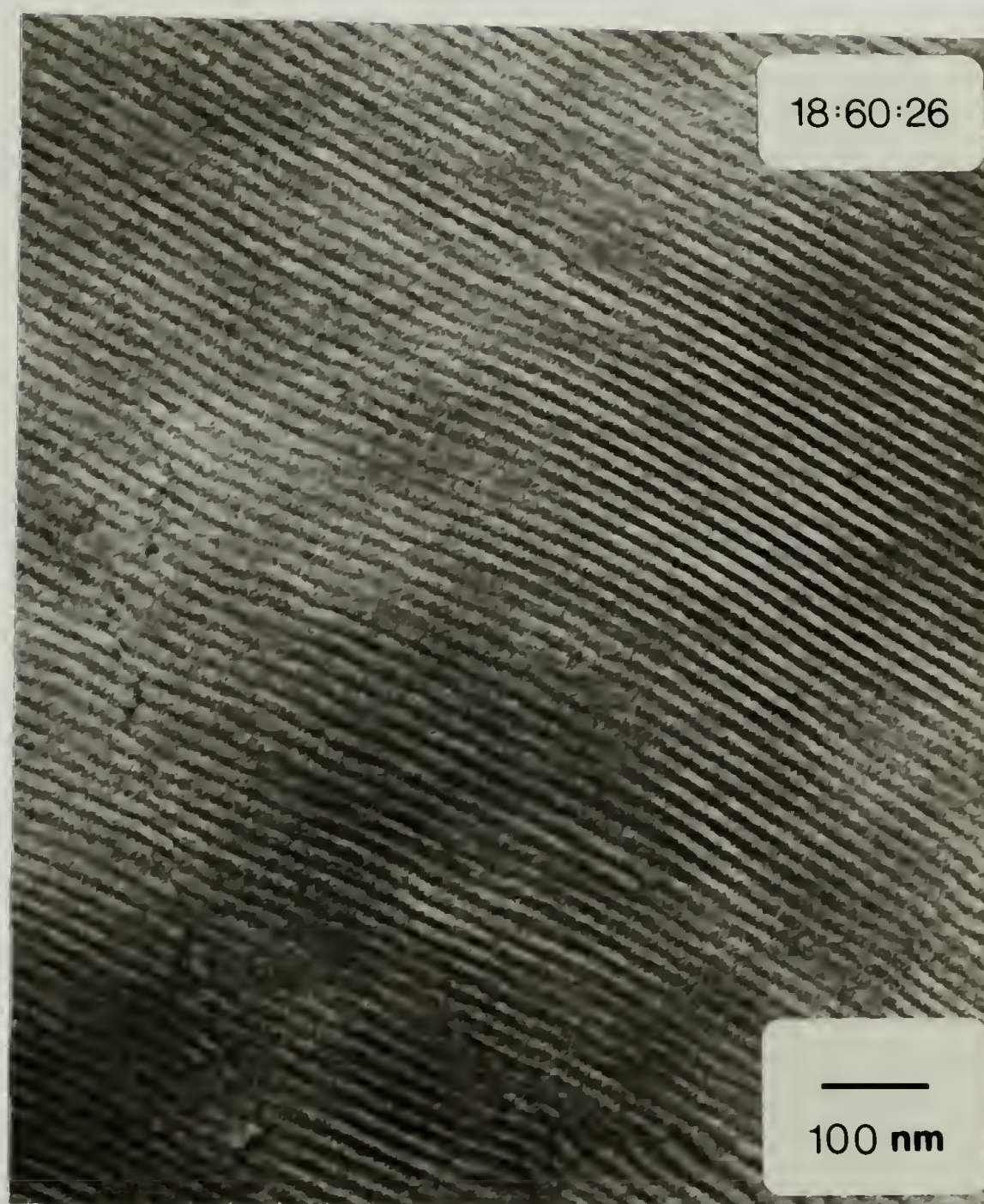


FIGURE 4.11 18:60:26 sample displaying lamellar morphology.

indicating that a phase inversion has occurred making the isoprene the discrete phase. Increasing the styrene content another 10% does not change the observed morphology. The 18:80:30 sample seen in Figure 4.13 again shows the cylindrical morphology. The cylinders seen in the 18:80:30 sample are smaller than those seen in the 18:70:30.

The 18:90:30 sample in Figure 4.14 shows spheres of isoprene in a matrix of styrene. This sample shows good long range order and regular packing of the spheres. The sphere diameter is approximately 140 Å. One interesting lesson can be learned by looking at Figure 4.15 also of sample 18:90:30. Because isoprene is the minor component, one would expect to see exclusively dark spheres. In area A of this micrograph however, one sees an apparent phase inversion suggested by the white spheres. This can be understood in terms of sample folds and tilt-projection effects. The microscopist must carefully consider what may seem obvious at first glance.

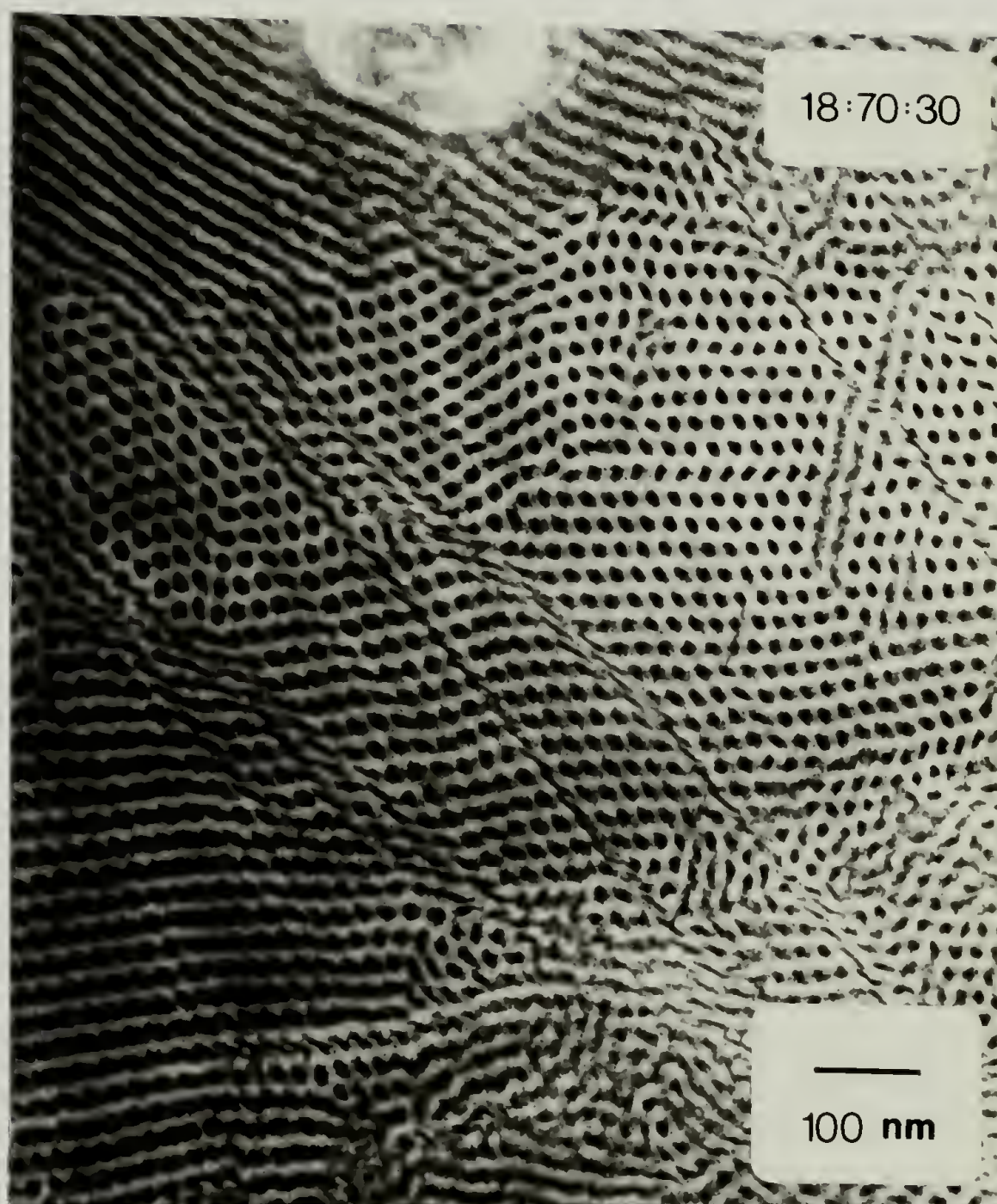


FIGURE 4.12 Cylindrical morphology as seen for the 18:70:30 sample.

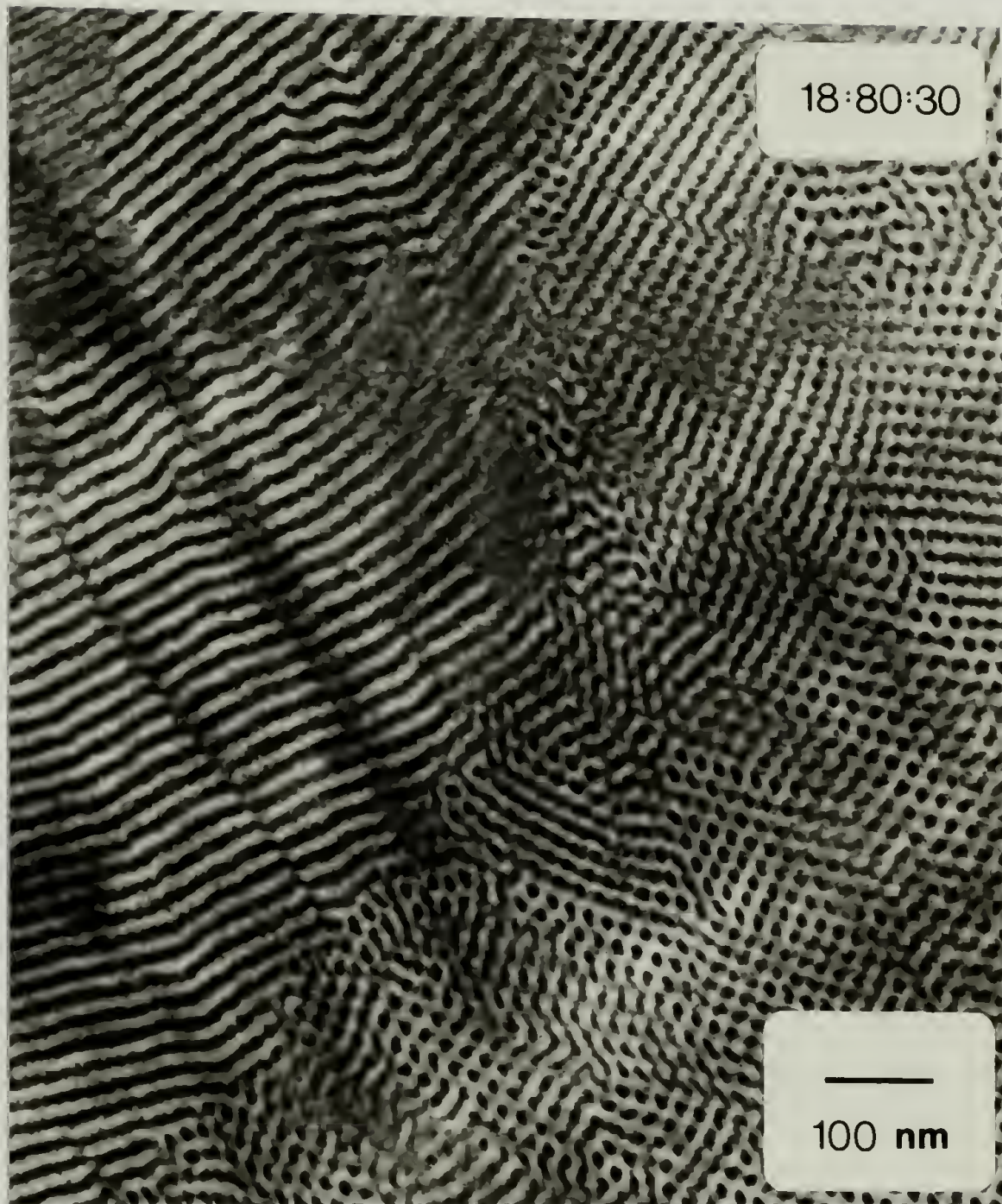


FIGURE 4.13 18:80:30 sample showing cylindrical morphology.

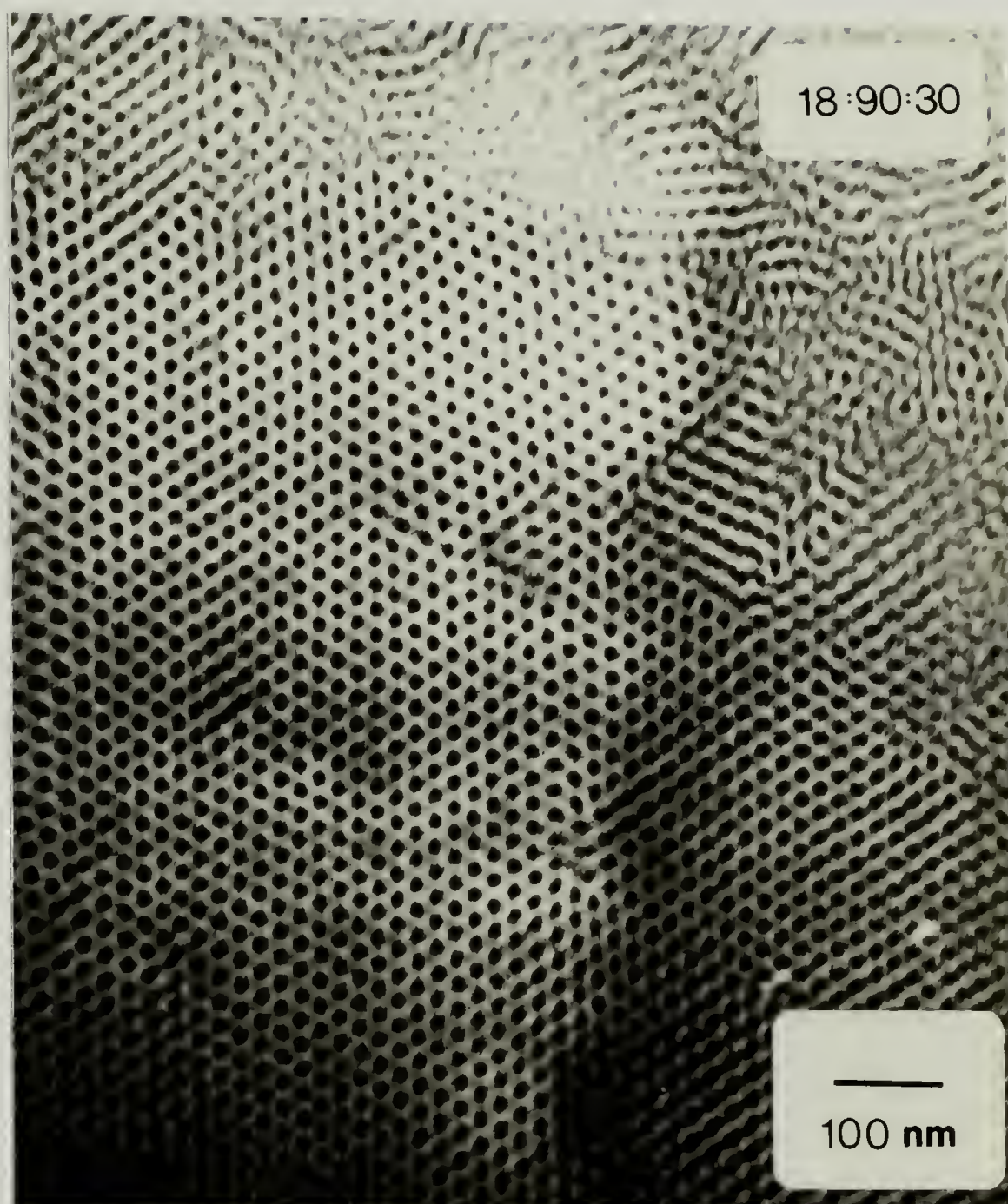


FIGURE 4.14 18:90:30 sample showing spherical morphology with good long range order.

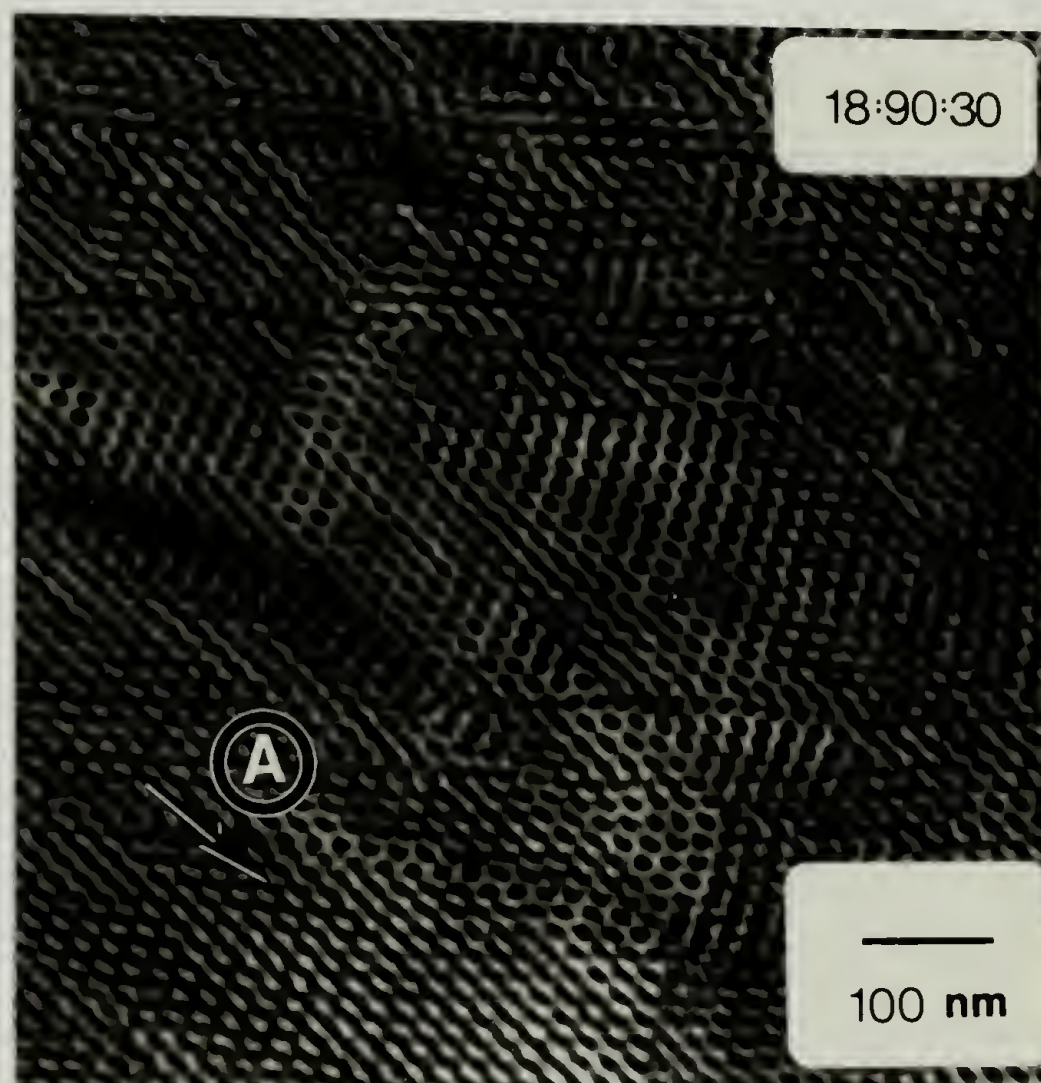


FIGURE 4.15 18:90:30 sample showing apparent phase inversion due to sample irregularities and tilting effects.

C H A P T E R I V

CONCLUSIONS AND FUTURE WORK

5.1 Conclusions

The observed morphologies for the eleven star diblock copolymer compositions are summarized in Table 5.1. The reader is referred to Figure 5.1 for a comparative collage of the previously exhibited micrographs. Sample compositions were chosen to represent a wide range of styrene content (10 to 90 %) with smaller intervals around the 30% sample which displays the OBDD structure (27, 33 and 36% polystyrene) in order to more closely define the cylinder-OBDD-lamellar transition. A schematic depicting the morphology as a function of composition for the star-block copolymers examined in this study appears in Figure 5.2.

The morphological transitions for lamellae, cylinders and spheres can be reasoned in terms of the relative block lengths of the star arms, the chain packing within the domains, and the curvature of the AB interface. For lamellar microstructures, a planar interface is seen since the two blocks are nearly equal in molecular volume. Blocks on either side of the interface have similar space limitations leading to a flat domain boundary. As the difference between the relative molecular volume of the two blocks increases, the interfacial surface must curve to satisfy the different space requirements for the two components. The larger block appears on the convex side of the interface where there is

**TABLE 5.1 OBSERVED MORPHOLOGIES OF
STAR BLOCK COPOLYMERS**

SAMPLE	MORPHOLOGY
18:10:10	SPHERES
18:20:10	CYLINDERS
18:27:12	CYLINDERS
18:30:10*	DOUBLE DIAMOND
18:33:10	DOUBLE DIAMOND+
18:36:10	DOUBLE DIAMOND
18:40:10	LAMELLAE
18:50:10	LAMELLAE
18:60:26	LAMELLAE
18:70:30	CYLINDERS
18:80:30	CYLINDERS
18:90:30	SPHERES

*From Reference 44.

+Not highly ordered.

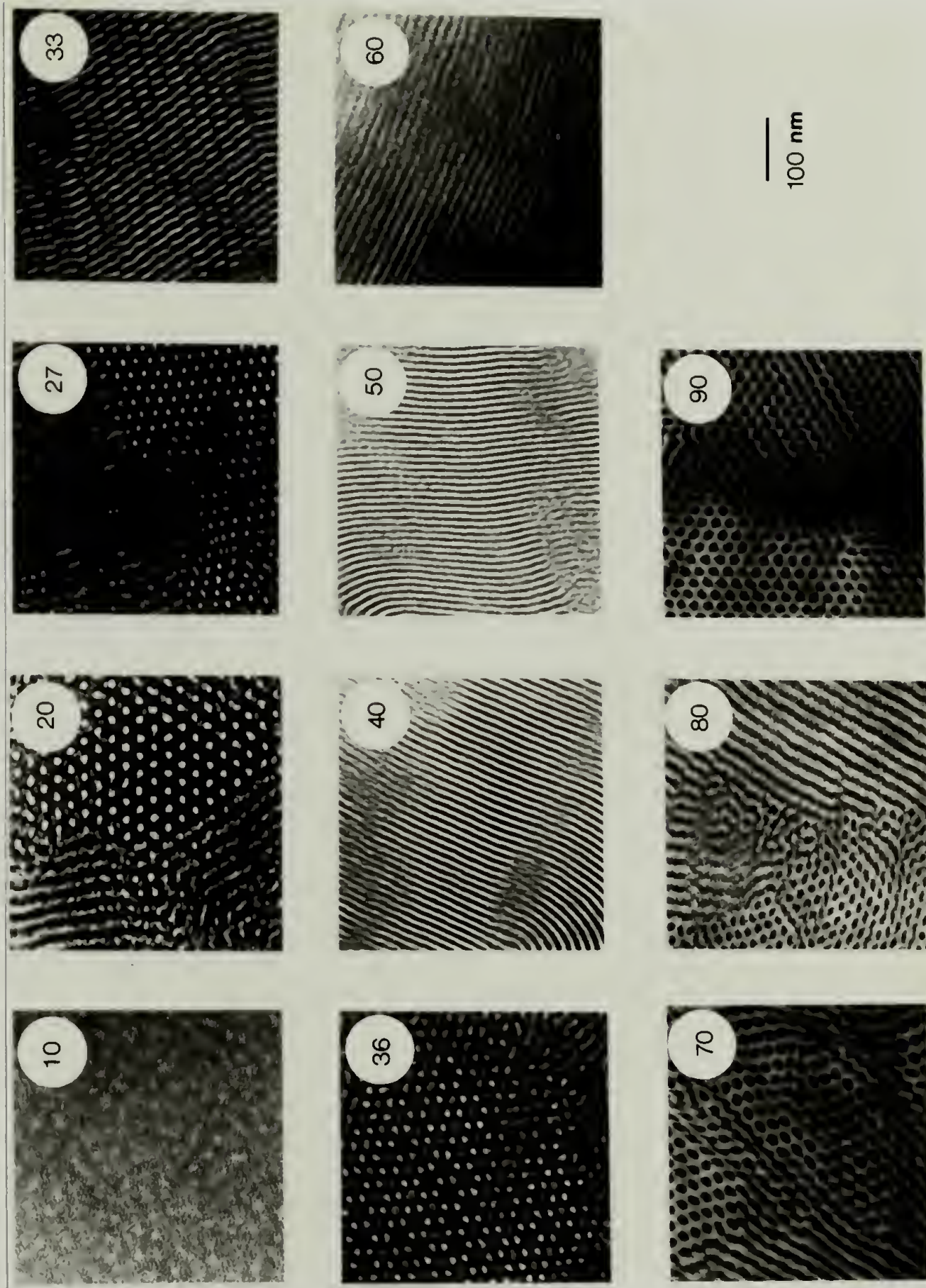


FIGURE 5.1 Summary of results as seen in the micrographs reported in the results section.

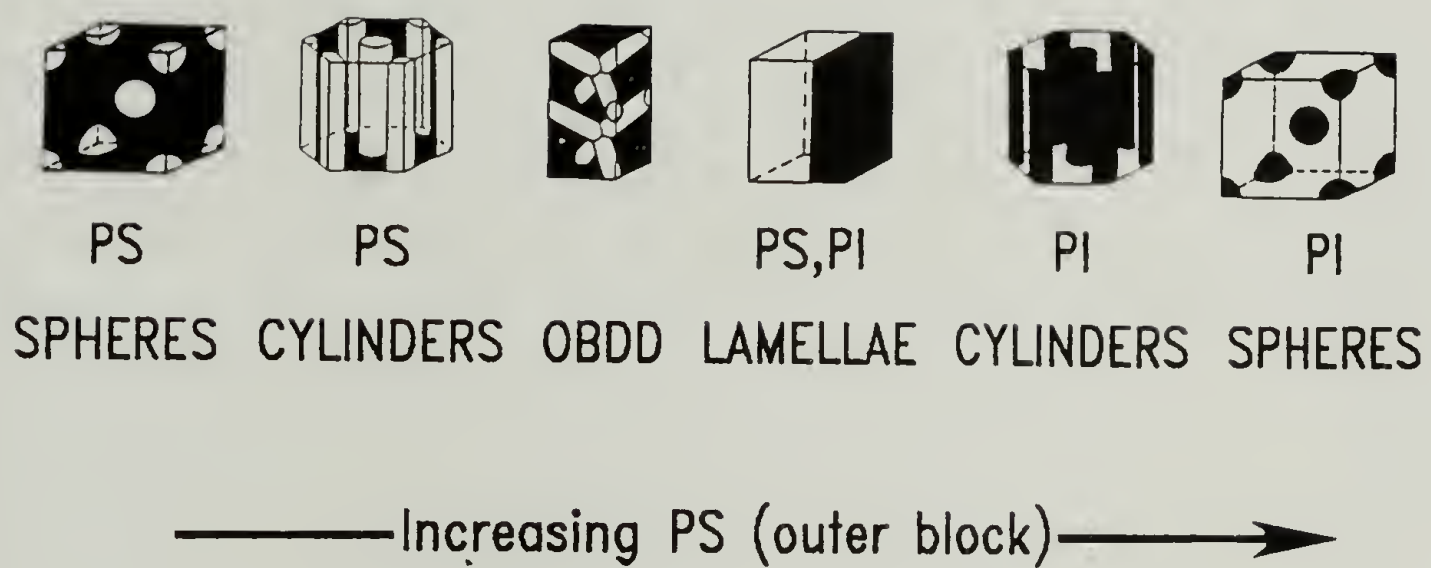


FIGURE 5.2 The compositional dependence of poly(styrene-isoprene) star block copolymers.

more space while the smaller block forms cylinders or spheres on the concave side [38].

5.2 Future Work

The annealing temperature of 120° may have been too high to help increase the long range order above that of as-cast films. A recent hypothesis by de la Cruz and Sanchez [48] suggests that there may be an upper critical temperature at which point the system exists as one phase rather than two. Maintaining a temperature above this obviously would not increase the order. Order then becomes dependent on the cooling rate following annealing. If there is an upper critical temperature for phase separation, then the greatest ordering would occur when the system is held just below that temperature. Work needs to be done to find this critical temperature so that annealing can promote maximal long range order.

The solvent casting conditions used in this study may have had a negligible effect on the establishment of long range order. The samples which had solvent drawn off slowly at elevated temperatures showed no better domain formation than those cast more quickly. Alward [44] had noted that annealing of high arm MW stars did little to promote order beyond that developed in the as-cast films. An alternate film preparation method such as casting films thin enough to be viewed directly under the microscope might show interesting results although

one might not get bulk morphologies. This would eliminate any deformation or residual stresses induced through microtomy.

The high MW of the 18-arm stars due to the large number of arms and/or high arm MW may inhibit domain formation due to hindered mobility. Since it was recently seen that a transition took place from the cylindrical to double diamond structure between 5 and 6 armed stars [40], it might prove useful to repeat this composition dependence of microphase separated states at a lower arm number i.e. 8- to 12-armed stars. These samples might form better equilibrium structures due to reduced overall molecular weight and lower arm number leading to fewer physical entanglements and higher chain mobility.

The sample compositions examined were chosen to represent a wide range of styrene content (10 to 90%) with a closer look in the neighborhood of the 30% sample which displays the OBDD structure. Indeed a composition window from 30 to 36% polystyrene outer block was established for OBDD. More detailed work in the composition range of the other morphological transitions (spheres to cylinders, lamellae to cylinders, OBDD to lamellae) might provide very useful information. The spherical to cylindrical transition could be explored by examining additional 18 arm samples in the 10 to 20% and 80 to 90% polystyrene range.

In addition to compositional effects on the morphology of star-block copolymers, functionality is known to play a role [44,45], and molecular weight most probably has an effect as well. For diblock systems, Leibler predicts that morphology is a function of the

composition, molecular weight and the interaction parameter for the polymer pair. For linear and star systems, this MW dependency needs to be further explored.

Analogous experiments for a series of star-diblocks which have an inverted structure (styrene at the core of the star with isoprene at the free end) would be interesting as a comparison. Other workers in our group have explored an 18 arm inverted star (18:76:47) and found the double diamond morphology for this 24 wt% polyisoprene outer block sample [38].

Small angle x-ray scattering would be an excellent technique to supplement the results reported in this thesis. The scattering data would confirm the microstructure and yield more accurate domain measurements since the X-ray scattering samples would not be subjected to swelling from the OsO_4 staining or dimensional changes induced by microtoming and the electron beam. Dynamic Mechanical Thermal Analysis (DMTA) would be useful to gain information about the relative moduli of the different morphologies. This method might also be of use in probing whether the glass transition temperature of the isoprene phase would reflect the changes in morphology.

Recent work on the surface structure of diblock copolymers has shown that the rubber phase always appears exclusively at the outer surface of the sample regardless of the morphology seen in the bulk of the material [49]. Further analysis of this phenomenon in reference to

the arm number, arm MW and total MW would be of interest for star-diblocks and inverted star-diblocks. Stars with the rubber component at the core would be most interesting.

Plastic deformation and fracture behavior of samples of the double diamond morphology is a completely unexplored area. Since the double diamond is such a rigid structure, one might gain more evidence supporting this model based on whether the fracture occurs intragranularly (i.e. within a domain) or at a grain boundary. One might observe for example, the double diamond morphology undergoing deformation using a deformation stage in the electron microscope as has been possible for polyethylene film [51].

One final suggestion to explore would be the morphology of star copolymers whose arms are tri-blocks rather than diblocks. One such sample (an 18:30:10.5 SIS) was looked at by this researcher. At this composition (30 wt% PS, one would expect to see cylinders for a linear di- or triblock copolymer sample. Stars with diblock arms and functionality of six or more display the OBDD structure. The 18 arm star block with triblock arms showed phase separation although no long range order was apparent. A lower number of arms for these types of samples would probably be necessary here as well to achieve near-equilibrium morphologies.

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